Imaging Reaction Dynamics of Y+SO₂†

Dong Yan, Yu-je Ma, Fang-fang Li, Jia-xing Liu, Guan-jun Wang, Feng-yan Wang*  
Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Fudan University, Shanghai 200433, China

(Dated: Received on March 8, 2020; Accepted on March 30, 2020)

The reaction dynamics of yttrium atoms with sulfur dioxide molecules at a high collision energy of 36 kcal/mol was studied using time-sliced velocity map ion imaging, crossed molecular beam and laser-ablation method. The product YO was detected via multiphoton ionization at various wavelengths in the region of 482–615 nm. The slice images of YO show a broad velocity distribution and forward-backward peaking angular distribution. The forward scattering signal is stronger than its backward distribution. This indicates that the reaction proceeds via an intermediate complex and the lifetime of the intermediate state is less than one rotational period. The formation of complex suggests that electron transfer occurs in the oxidation reaction.

Key words: Time-sliced velocity map imaging, Crossed-beam, Laser ablation, Metal atom reaction dynamics, SO₂

I. INTRODUCTION

Oxidation reaction is an important branch in chemical reactions in which reactants begin their chemical interactions by electron transfer. We have discussed the harpoon mechanism, the long-range electron transfer during the oxidation of aluminum atoms in the gas phase [1], where metal atoms use their valence electrons as “harpoons” to attract oxygen molecules and form an AlO₂⁻ complex followed by rapid decomposition. For IIIB transition metal atoms, Sc, Y, and lanthanides have (n–1)d¹ns² (2D) configuration and low ionization energy, and can form strong bonds with oxygen atoms. Recently, the oxidation reaction dynamics of the gas-phase yttrium atoms by oxygen molecules has been studied under crossed-beam and ion imaging conditions [2, 3]. The forward-backward symmetry observed in the angular distribution of YO products indicates that the oxidation reaction proceeds via long-lived intermediates.

Among the oxidant molecules, SO₂ is one of the main pollutants in the atmosphere [4]. It can be expected that due to the positive electron affinity for SO₂ (1.1 eV) [5], the reaction between SO₂ and metal atom occurs through an electron transfer mechanism. Smith and Zare used laser-induced fluorescence (LIF) to study the spin-forbidden reaction of Ba(S⁺) + SO₂(X^1A) → BaO(X^1Σ⁺) + SO(X^3Σ⁻), and proposed that the long-lived Ba⁺SO₂⁻ complex helps the singlet-triplet transition through spin-orbit or spin-rotation coupling [6]. Spence et al. studied the chemiluminescence spectra of the electronically excited MnO products generated by the reaction of excited Mn atoms with SO₂, and proposed that electron transfer occurred at short internuclear distances [7]. Costes and coworkers studied the reactive collisions of aluminium atoms with SO₂ in the crossed molecular beams and LIF experiment, and found that the change in reactive cross section with collision energy was consistent with the harpoon mechanism [8]. Liu and Parson used the LIF method under beam-gas conditions to study the rovibrational distribution YO(X^2Σ⁺) products from the reaction of Y with SO₂, and suggested that the reaction also proceeded via long-lived complexes [9].

In this work, we use the crossed-beam, time-sliced velocity map ion imaging, and laser multiphoton ionization to study the reaction, Y(a^2D) + SO₂(X^1A₁) → YO(X^2Σ⁺, A^2Π or A^2Δ) + SO (X^3Σ⁺, a^1Δ or b^3Σ⁺). For the Y atom, the spin-orbit split energy difference between 2D₃/₂ and 2D₅/₂ is 530 cm⁻¹, and the lowest excited state has a high excitation energy of 10529 cm⁻¹ [10], indicating only 2D state under molecular beam cooling condition involved in the oxidation reaction. Complementing previous LIF spectroscopy studies [9], the speed and angular distributions of products will help further to clarify whether the reaction proceeds through a long-lived complex mechanism or directly, and whether the ground state product and the excited state product originate from the same reaction mechanism or not.

†Part of the special topic on “The International Conference on Molecular Energy Transfer in Complex System (2019)”.
*Author to whom correspondence should be addressed. E-mail: fengyanwang@fudan.edu.cn

DOI:10.1063/1674-0068/cjcp2002029
II. EXPERIMENTS

In this experiment, the crossed-beam apparatus combined with time-sliced ion velocity imaging detection was used [1, 11–16]. Yttrium atoms were generated by laser-ablation of yttrium rod (97% Y, Alfa) with a focus lens (f=350 mm) at the laser wavelength 532 nm (1–3 mJ/pulse), which was generated by double-frequency of the Continum Minilite II. The supersonic Y beam (speed of ~2600 m/s) was formed by using pure hydrogen molecules as carrier gas, expanding from an Even-Lavie valve (pulse width of ~24.5 μs) and entering into the main vacuum reaction chamber. Sulfur dioxide molecular beam (speed of ~1000 m/s) was formed from another Even-Lavie valve (pulse width of ~29.5 μs), in which helium was the carrier and the concentration was ~14%. Both molecular beams were collimated by a skimmer (Beam Dynamics Model No.50) and crossed each other at a right angle at the center of the ion optics system, where the reaction products were ionized. The ionization laser beam was generated from a 355 nm Nd:YAG laser pumped Continum Sunlite OPO/OPA laser with a pulse width of 5–9 ns and a pulse energy of 4–6 mJ. A focusing lens (f=500 mm) was used along the propagation direction of the probe beam, which propagated in the plane of the atomic and molecular beams and bisected the right angle made by the Y and SO$_2$ beams. Under the action of the ion optics system with a total voltage of 3200 V, the product ions were accelerated and projected by the ion optics onto the position-sensitive detector. The detector was composed of two micro-channel plates (75 mm, 60:1, 10 μm pores, and 12 μm pitch, Photek) and one Phosphor Screen (P43, Photek). The photon signals emitted from P43 were recorded by the Lavision Elite CCD camera and transferred to a computer where the images were accumulated and processed. Sliced images were recorded by applying a 30 ns gate pulse onto the detector. The background subtraction scheme was to sequentially open and close the SO$_2$ beam for data acquisition to remove the YO background ablated on the Y rod due to the oxide contamination.

III. RESULTS AND DISCUSSION

As shown in FIG. 1(a), according to the energetics data of the Y+SO$_2$ reaction, YO or SO products in the ground state and electronically excited states can be formed at the collisional energy of 36 kcal/mol. Several low electronic states of YO, including $X^2\Sigma^+$, $A^2\Delta_{3/2,5/2}$ (14531 cm$^{-1}$, 14870 cm$^{-1}$) and $A^2\Pi_{1/2,3/2}$ (16315 cm$^{-1}$, 16742 cm$^{-1}$), are energetically allowed when SO lies in the $X^3\Sigma^-$ and $a^1\Delta$ (6344.79 cm$^{-1}$) states [17]. However, for SO in the excited $b^1\Sigma^+$ (10507.8 cm$^{-1}$) state, only YO in the ground state $X^2\Sigma^+$ is allowed. The spectroscopic constants of the YO and SO in the related electronic states are shown in Table I [17, 18]. In our YO detection scheme, the ground state YO($X^2\Sigma^+$) product can be probed via (1+2) multi-photon ionization at ~482.116 nm (20741.9 cm$^{-1}$), through $B^2\Sigma^+$ as the intermediate state, and the exited state YO ($A^2\Delta_{3/2}$, $A^2\Delta_{5/2}$, $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$) products can be probed via (2+1) multi-photon ionization at ~577.048 nm (17329.6 cm$^{-1}$), ~582.751 nm (17160 cm$^{-1}$), ~607.434 nm (16462.7 cm$^{-1}$) and ~615.998 nm (16233.8 cm$^{-1}$), respectively, with the Rydberg state (~49191 cm$^{-1}$) as the intermediate state. The ro-vibrational state of YO can be ionized by scanning...
adjacent wavelengths. The ionization energy of the ground state of YO molecule is 6.11 eV (49281.6 cm$^{-1}$) [19]. The slice images of YO products at different wavelengths after background subtraction are shown in FIG. 1(b). The background of the YO beam ablated from the Y metal rod lies in the flying direction of the Y beam. Each slice image of the YO products shows a backward and forward peak angular distribution in the center-of-mass coordinate. The almost identical images at different wavelengths indicate that the internal state distribution of YO+SO coproducts cannot be well-resolved. From the slice images, we obtained the velocity distributions, which were determined by the accumulation of the signals between 90$^\circ$ and 270$^\circ$ (without the background pollution) in the center-of-mass coordinate.

FIG. 2 shows the total kinetic energy release (TKER) distributions, which were converted from the speed distributions of YO products according to the conservation of recoil momentum. The TKER distributions measured at the five wavelengths all displayed a broad distribution, up to nearly 2000 cm$^{-1}$ and peaked at around 7000 cm$^{-1}$. The available energy ($E_{\text{total}}=E_r-\Delta H$) for the reaction system is approximately 24348 cm$^{-1}$ ($\Delta H$ is derived for ground state products, from $D_0$(SO−O)=540.326 kJ/mol [18] and $D_0$(Y−O)=715.11 kJ/mol [20], consistent with the observed maximum total kinetic energy. In molecular beam experiments, supersonic cooling after laser ablation of metal rod can quench highly excited atoms by frequent collisions with carrier gas. However, we cannot rule out the existence of the spin-orbit excited state of YO($a^2D_3/2$), which is only 530 cm$^{-1}$ higher than the ground state YO ($a^2D_3/2$). Assuming that the coproduct SO is in the states of $X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$, the internal energy states of YO are shown on the top labels of FIG. 2 (a), (b) and (c), respectively. The maximum TKER is consistent with the channel of FIG. 2(a) for SO($X^3\Sigma^-$). The TKER of the products peaks at 7000 cm$^{-1}$, which is about 15000 cm$^{-1}$ less than the maximum TKER. This is consistent with the energy required for electronic excitation of YO molecules. The high vibrational excitation of YO products also contributes to the small TKER. Kopin Liu et al. have shown that the lifetime of the $A$ state is very short, about 30$-$40 ns [9], which is much shorter than the accumulative reaction time of tens of microseconds, and most of the YO($A$) products formed before the ionization laser emit fluorescence and return to the ground state YO($X$). Therefore, with a short-pulsed laser width of about 10 ns, only a small portion of the YO($A$) products can be ionized directly from the nascent products. However, since the ionization efficiency of the ground state and excited state cannot be obtained at the current probe wavelengths, we cannot obtain detailed information about the internal energy distributions of products.

Since the raw images are very similar at various wavelengths, the combined image and the corresponding speed and angular distributions are used for further analysis and discussions. FIG. 3 shows the speed distribution and angular distributions of the YO products in the combined image. The angular distribution signals were integrated in the speed range of 500$-$700 m/s and 1000$-$1050 m/s, respectively. The low-speed range is mainly composed of the excited electronic state YO or highly vibrationally excited YO($X$), while the high-speed range mainly corresponds to the low vibrational levels of YO($X$). The high-speed forward YO signal is

| TABLE I Spectroscopic constants for YO and SO. Units are given in cm$^{-1}$ (taken from Refs.[17, 18]). |
|-----------------|-----------|------------|--------|--------|
| YO              | $X^2\Sigma^+$ | $a^1\Delta$ | $b^1\Sigma^+$ |
| $T_e$           | 0         | 861.0      | 10510.0       |
| $\omega_e$      | 2.93      | 3.62       | 7.2       |
| $\omega_{\chi_e}$ | 0.3881    | 0.3857     | 0.7026    |
| $B_e$           | 0.0018    | 0.0023     | 0.0063    |
| $\alpha$        | 0.7103    | 0.7208     | 0.7026    |

FIG. 2 Total kinetic energy distributions of YO+SO products at various ionization wavelengths. The labels on the top of the figure (a), (b), and (c) correspond to the vibrational levels of YO in different electronic states when SO products are defined as the electronic state of $X^3\Sigma^+$, $a^1\Delta$ and $b^1\Sigma^+$, respectively.

DOI:10.1063/1674-0068/cjcp2002029 ©2020 Chinese Physical Society
and angular distributions were determined by the time-sliced ion velocity imaging. The angular distributions show a forward-backward asymmetry with forward peak dominating, which indicate that the reaction proceeds through an intermediate complex and that the lifetime of the intermediate state is less than one rotational period. The formation of complex suggests that electron transfer occurs in the oxidation reaction. Theoretical calculations are required to understand more on the reaction mechanism.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.21673047, No.21327901 and No.21573047), the Shanghai Key Laboratory Foundation of Molecular Catalysis and Innovative Materials, and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.